REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
07-12-2012	Final Report	1-Sep-2009 - 31-Aug-2012

4. TITLE AND SUBTITLE
FINAL REPORT

5a. CONTRACT NUMBER
W911NF-09-1-0486

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Rodney J. Bartlett

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Florida - Gainesville
Office of Sponsored Program
University Of Florida
Gainesville, FL 32611 -

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
54344-CH.8

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Ab initio coupled-cluster theory applied to nitramine explosives RDX, HMX, and CL20. Isomers identified, and follow-up work will focus on transition ststes and activation barriers for decomposition. All applications are made possible by the development of the massively parallel ACES III program system, that runs highly efficiently on the DoD High-Performance Computer Systems. The other direction for this project is to organize most explosive molecules in terms for their functional groups, using localized orbitals and the natural liner scaling coupled-cluster

15. SUBJECT TERMS
ab initio theory, nitramines, deflagration to detonation, RDX, HMX. CL20, coupled-cluster theory

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Rodney Bartlett
UU	UU	UU	UU		19b. TELEPHONE NUMBER: 352-392-6974

Report Title

FINAL REPORT

ABSTRACT

Ab initio coupled-cluster theory applied to nitramine explosives RDX, HMX, and CL20. Isomers identified, and follow-up work will focus on transition ststes and activation barriers for decomposition. All applications are made possible by the development of the massively parallel ACES III program system, that runs highly efficiently on the DoD High-Performance Computer Systems. The other direction for this project is to organize most explosive molecules in terms for their functional groups, using localized orbitals and the natural liner scaling coupled-cluster approach.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/30/2011	1.00	Rodney Bartlett, Victor Lotrich, Thomas Watson, Robert Molt. RDX Geometries, Excited States, and Revised Energy Ordering of Conformers via MP2 and CCSD(T) Methodologies: Insights into Decomposition Mechanism, Journal of Physical Chemistry A, (01 2011): 884. doi:
12/07/2012	6.00	Robert W. Molt, Alexandre Bazanté, Thomas Watson, Rodney J. Bartlett. Pragmatic ab initio prediction of enthalpies of formation for large molecules: accuracy of MP2 geometries and frequencies using CCSD(T) correlation energies, Journal of Molecular Modeling, (11 2012): 0. doi: 10.1007/s00894-012-1663-1
TOTAL:	**2**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

June 2012 – Coupled-Cluster Theory and Related Methods, a satellite meeting of the 2012 International Congress of Quantum Chemistry, Boulder, CO

September 2012 – 3rd Conference on Theory and Applications of Computational Chemistry, Pavia, Italy

September 2011 – 10th Central European Symposium on Theoretical Chemistry (CESTC 2011), Torun, Poland

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
12/07/2012	5.00	R. W. Molt, A. Bazante, T. J. Watson, R. J. Bartlett. The grezt diversity of HMX conformers: Probing the PES using CCSD(T), ( )
12/07/2012	7.00	. .Conformers of CL-20 Explosive and ab initio Refinement using Perturbation Theory; Implications to Detonation Mechanisms, ( )
TOTAL:		**2**

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Doctor Honoris Causa, Comensius University, Bratislava, Slovakia, October, 2012.

Dcctor of Science, Honoris Causa, Millsaps College, Jackson, MS, May, 2011.

Southern Chemist of the Year, ACS, Memphis, TN, January, 2010.

American Chemical Society, Fellow, 2010

S.F. Boys – A. Rahman Award from the Royal Society of Chemistry 2009/2010

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Tom Watson	0.20	
Robert Molt	0.67	
Alex Bazanta	0.00	
Ann Melnichuk	0.20	
FTE Equivalent:	**1.07**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Victor Lotrich	0.20
Dmitry Lyakh	0.33
FTE Equivalent:	**0.53**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Rod Bartlett	0.12	No
FTE Equivalent:	**0.12**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Tom Watson
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The work we have done under this grant has resulted in a number of advances in the field, and started a few others that we will continue to pursue in the future.

- Definitive studies of the ground state potential energy surfaces for the nitramine molecules RDX, HMX, and CL20 at the highest applicable level of ab initio, correlated, electronic structure theory: coupled-cluster (CC) theory with triple excitations, CCSD(T). The objective is to find all the energetically accessible isomers and associated activation barriers that would describe the energetic and kinetic effects on their detonation and decomposition.
- Investigation of low-lying excited states using the equation-of-motion (EOM) CC. This aspect is also important in understanding the critical initial steps from deflagration to detonation. In most processes sufficient energy will exist to excite a molecule into its electronic excited states, whether done by shock or by photon excitation, which opens new pathways toward deflagration.
- Introduction of a new way to begin to organize the chemistry of energetic materials, based upon their functional groups. Using the nitramines as prototypes, the idea is to be able to organize and understand most of the critical properties of the isolated molecules in terms of transferable *CH2-N-NO2 units. The * means an artificial bond to a 'link' atom that accommodates all valences in the methyl nitramine group, to enable it to assume its normal electron pair bonding patterns. By using the ideas of the Natural Linear Scaling Coupled-Cluster (NLSCC) method, a transformation to local orbitals is expected to sufficiently separate the different functional groups into transferable units, that those units, say taken from RDX, will equally well describe HMX or CL20 without having to do the calculation for the whole system.
- This also means that all excited states of nitramines will be understood in terms of 3 units for RDX, 4 for HMX, and 6 for CL20. That classifies the excited states as intramolecular consisting of excitations within one nitramine unit or, intermolecular, between two units. If they occur, the completely delocal excited states would presumably involve all units, but the above classification should greatly aid in interpreting the spectra of the molecules.
- To the degree that the units are genuinely transferable, then stringing together many of them as building blocks would enable a description of even the crystalline form.
- Once the same procedure is used to separate other energetic units, like *CH2-NO2, eg, then the units can be combined together to build any molecule that is composed of nitramne and nitro groups. Extension to other units is apparent.
- This procedure potentially provides a way to represent the 'electronic structure' of all energetic molecules in terms of their component units, much as molecular mechanics provides the geometric structure of molecules based upon the force-fields that have been created

Technology Transfer